Overshoot in Photocurrent Rise Curve for TiO_2 Doped with Zn^{2+}

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A long duration of the overshoot of photocurrent was observed for TiO_2 doped with Zn^{2+}; the extent of the overshoot decreased on successive irradiation *in vacuo* or in the presence of oxygen, while it kept constant in the presence of hydrogen, indicating that the photo-desorption of hydrogen is responsible for the overshoot.

An overshoot in photocurrent rise curve has been observed only in limited cases such as CdS[1,2] and CdSe.[2,3] Bube *et al.*[1] and Weiss *et al.*[2] have asserted that the photocurrent overshoot is caused by the existence of two types of recombination centres in which the rates of recombination between the holes and electrons are different. We previously reported that a slight overshoot was observed for TiO_2.[4] Now, we report that the overshoot becomes much more clearly observed as TiO_2 is doped with Zn^{2+}, and that the cause for the overshoot is different from the one observed for CdS and CdSe. The overshoot duration was 5—30 s for Zn^{2+}–TiO_2 in contrast to 20—30 ms for CdS and CdSe.

The Zn^{2+}–TiO_2 was prepared by soaking TiO_2(anatase) in an aqueous solution containing 0.5 mol % $ZnCl_2$, followed by drying and calcining at 1273 K for 1 h in air. Before measurement of the photocurrent, the sample was reduced at 773 K for 2 h in a hydrogen stream flowing at 200 cm^3 min^{-1}. Photo-irradiation for 60 s was repeated every 60 min. The photocurrent was measured at room temperature *in vacuo*, and in the presence of 200 Pa hydrogen or oxygen.

The photocurrents observed in different atmospheres as a function of time are shown in Figure 1. The photocurrent curves observed with TiO_2 without dopant are also shown in Figure 1. Addition of Zn^{2+} markedly increased the extent of

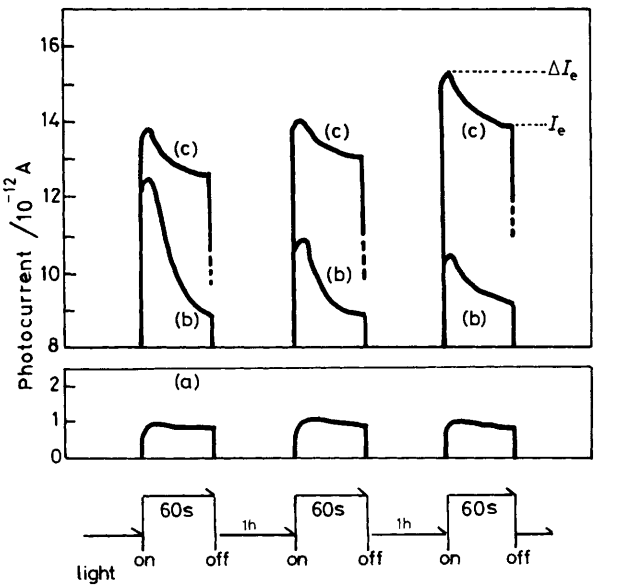

Figure 1. Photocurrent rise curves for repeated irradiation of (a) TiO_2 *in vacuo* and Zn^{2+}–TiO_2 (b) in O_2, (c) in H_2.

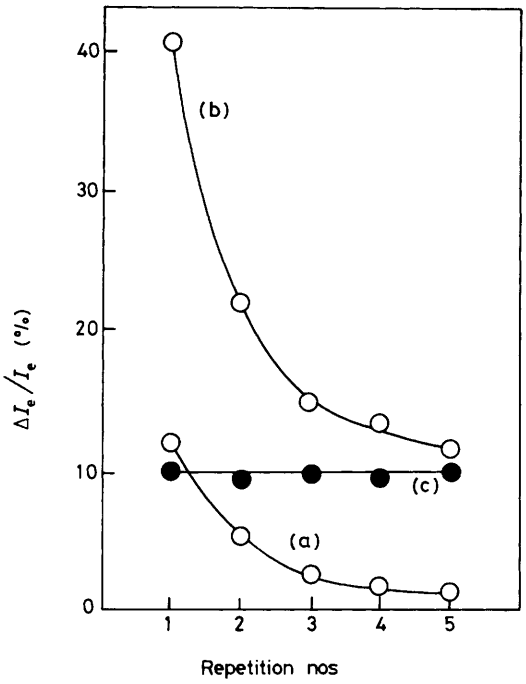

Figure 2. Variations in the extent of overshoot ($\Delta I_e/I_e$) as a function of the repetition number of photo-irradiation in the different atmospheres: (a) *in vacuo*, (b) in O_2, (c) in H_2.

overshoot. The duration of overshoot persisted for about 5—30 s. The overshoot changed with repetition of the irradiation, and these changes were also different for different atmospheres. In Figure 2, the extents of overshoot, expressed by $\Delta I_e/I_e$, are plotted against the repetition number of photo-irradiation under different atmospheres. The extent of overshoot decreased with the number of repetitions *in vacuo* and in the presence of oxygen, but kept constant in the presence of hydrogen.

To examine whether surface hydrogen is associated with the overshoot phenomenon, a hydrogen-free surface of Zn^{2+}–TiO_2 was obtained by exposing the surface to 2,2-diphenyl-1-picrylhydrazyl (DPPH) in benzene. DPPH reacts with surface hydrogen to produce 1,1-diphenyl-2-picrylhydrazine ($DPPH_2$) [reaction (1)].[4,5] With the hydrogen-free surface of Zn^{2+}–TiO_2, no overshoot phenomena were observed. This result, together with the constant extent of overshoot with repetition of irradiation in the presence of hydrogen, suggests that hydrogen is associated with the occurrence of the overshoot.

$$[S]\text{–}H + DPPH \rightarrow DPPH_2 + [S]\cdot \quad (1)$$

It is considered that the conduction electron for the overshoot phenomena is supplied by the photodesorption of hydrogen as shown in equation (2). The electrons generated by photodesorption of hydrogen gradually recombine with electron traps to decrease the photocurrent. *In vacuo* or in the

$$2[S]\text{–}H \rightarrow 2[S]^+ + 2e^- + H_2 \quad (2)$$

presence of oxygen, the amount of hydrogen on the surface decreases with the repetition of photo-irradiation, which results in a decrease in the extent of overshoot. In the presence of hydrogen, however, the surface hydrogen is regenerated by hydrogen adsorption in a dark process to give a constant extent of overshoot with the repetition of the irradiation.

A long duration of the overshoot observed for Zn^{2+}–TiO_2 explains that the chemical processes of hydrogen adsorption–desorption are involved in the overshoot phenomenon.

The role of Zn^{2+} ions in increasing the overshoot photocurrent is considered to provide the surface with hydrogen adsorption sites. Since hydrogen is strongly adsorbed on ZnO,[6,7] a large amount of the relevant hydrogen is retained on the surface of Zn^{2+}–TiO_2 following pretreatment with hydrogen. Thus, it is plausible that the adsorbed hydrogen is desorbed on photo-irradiation to cause the large overshoot of photocurrent for Zn^{2+}–TiO_2.

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